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QUARTERLY PROGRESS REPORT

STUDY OF SUSCEPTIBILITY OF SOLID COMPOSITE PROPELLANTS
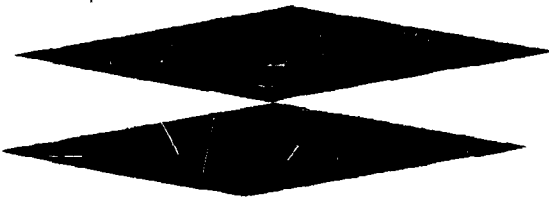
TO

EXPLOSION OR DETONATION

Task 4, Phase 2.

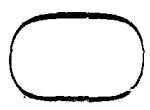0253-05(18)QP

15 June 1962 through 15 September 1962

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ORDNANCE DIVISION

Aerojet-General ®

CORPORATION

AEROJET-GENERAL CORPORATION
Ordnance Division
11711 Woodruff Avenue
Downey, California

STUDY OF SUSCEPTIBILITY OF SOLID COMPOSITE PROPELLANTS

TO

EXPLOSION OR DETONATION

Task 4, Phase 2.

0253-05(18)QP

Written by

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Period Covered:

15 June 1962 through 15 September 1962

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1. INTRODUCTION AND SUMMARY.

The contract pertains to the feasibility of controlling the sensitivity of propellants, particularly by surrounding them with a suitable gas. It is based on the arguments that shock in air produces certain species that are known to promote initiation of several explosives, and that this promoting effect occurs by chemical reaction on the surface of the explosive.

The first step in a study of this type should then be to establish whether the sensitivity of a given explosive may be affected at all by controllable conditions at its surface. Such controllable conditions are contact with a particular gas, contact with a particular metal, surface treatment with some material.

The work done in the period covered by this report has been limited to this first step. For experimental convenience a highly sensitive explosive (hydrazine perchlorate) was used. This can be obtained in powder form only. The effect of the surrounding gas is therefore hard to study, since it is hard to replace the air by the gas under study, and the results obtained so far are not conclusive. Experiments with different metals in contact with the explosive were more successful. These experiments show a considerable effect of the nature of the metal.

It seems, thus, that the first step in this study has been successfully accomplished, and that the feasibility of the control of the sensitivity of explosives by control of the surface conditions has been shown. In order to assess the technical value of this result, these experiments will be continued and further data gathered.

Impact tests have been conducted on hydrazine perchlorate in a small dropweight machine that can be used at the Downey facility. The machine permits introduction of various gases around the sample and inserts of various metals between sample and anvil and between sample and plunger.

The experiments with different gases have shown a great effect of moisture, which is peculiar to hydrazine perchlorate, but little other difference between the gases used. The following gases were used: ambient air, dried air, N_2 from the bottle, dried N_2, O_2, argon, and NO.

The experiments with different metals have shown conspicuously higher sensitivity with steel than any other metal tried. The following metals were used as inserts: none, copper, aluminum 99.5%, aluminum 99.99%, brass, stainless steel 304, stainless steel 410 of different heat treatments, spring steel 1095 of different heat treatments. Anvil and plunger were made of hardened plowsteel 1041. Whereas no insert gave initiation at a height of 25 cm, Cu, Al, and brass gave no initiation at 51 cm. The spring steel as received gave initiation at 41 cm, and as quenched from austenite (920°C) at 36 cm; after quench from austenite and subsequent tempering for one hour at 300°C it gave initiation at 21 cm. Cu and Al inserted above the sample only or below the sample only gave initiation, but not in both positions. Thus, Cu gave initiation at 49 cm when inserted above the sample, but did not give initiation at 51 cm when inserted below the sample.

These experiments have now been completed. The work will continue at the Chino facility where a taller machine has been made available. A tentative correlation, to be further studied, is that a reducing metal, like Cu or hydrogen-bearing steel, gives a lower sensitivity of hydrazine perchlorate than does low-hydrogen steel. This effect may be a result of reduction of shock products.

2.   EXPERIMENTAL PROCEDURE

For reasons of safety, security, transportation, and general experimental convenience, work of this type at the Downey facility is more efficient than work at the Chino facility. Accordingly, a small drop-weight machine was constructed for use at Downey. This machine had to be small enough to go into a laboratory fume hood. The maximum height of fall was thereby limited to 51 cm, and the weight was limited to 400 gm. This required a sensitive enough explosive. Hydrazine perchlorate meets this requirement. It was used exclusively in these experiments.

While experiments were conducted at Downey, the dropweight machine at Chino was modified and reassembled. It permits a maximum height of fall of 66 in., using a standard 2 kg weight. This machine will be used for experiments with the same explosive under conditions of reduced sensitivity.

Figure 1 shows the principles of the small dropweight machine used at Downey. A cylindrical hardened steel weight of 400 gm is made to impact upon a plunger in contact with the explosive. The dropweight is held in a tube, which serves as a guide, by means of a pin that can be pulled out by an electromagnet. In order to avoid repeated bouncing, the dropweight carries a spring assembly that is released by the impact and prevents movement downwards. The pin that holds the dropweight fits in holes in the tube, spaced 1 in. apart.

The plunger, shown in detail in Figure 1, is made such as to permit flushing of the chamber in the anvil. The flushing gas is introduced through a hole in the anvil and escapes through the space between anvil and plunger. The fit of the plunger in the hole in the anvil is too snug to permit the escape of the gases evolved in detonation. For the rapid escape of these gases, 12 holes of 2.4 mm diameter have been drilled through the plunger as shown in Figure 1. These holes are covered by a ring-shaped aluminum foil. The detonation punches holes in this foil, and the foil thus gives indication of detonation.

The hydrazine perchlorate (HP) is desensitized for shipping by wetting with carbon tetrachloride. Before use, this agent must be driven off. The HP must thereby be carefully protected against water. HP picks up water readily from the air and forms then a comparatively insensitive hydrate. The samples were prepared by drying in vacuum for one day and then stored overnight in a desiccator. The samples were kept in the desiccator until loaded into the machine. Samples prepared in this manner had a suitable sensitivity and were uniform as to sensitivity to impact.

The same volume of sample was used in all the tests. It was measured with a little scoop. The sample weight was approximately 25 mg. The sample was placed as a pile in the center of the chamber. A thin layer of the powder was much less sensitive.

Most of the experiments were conducted with ambient air around the sample. The absorption of water by the sample in the short period of exposure to the ambient between storage in the desiccator and initiation was negligible. This point is proved by the fact that the sensitivity was the same when the ambient was flushed out with dried air.
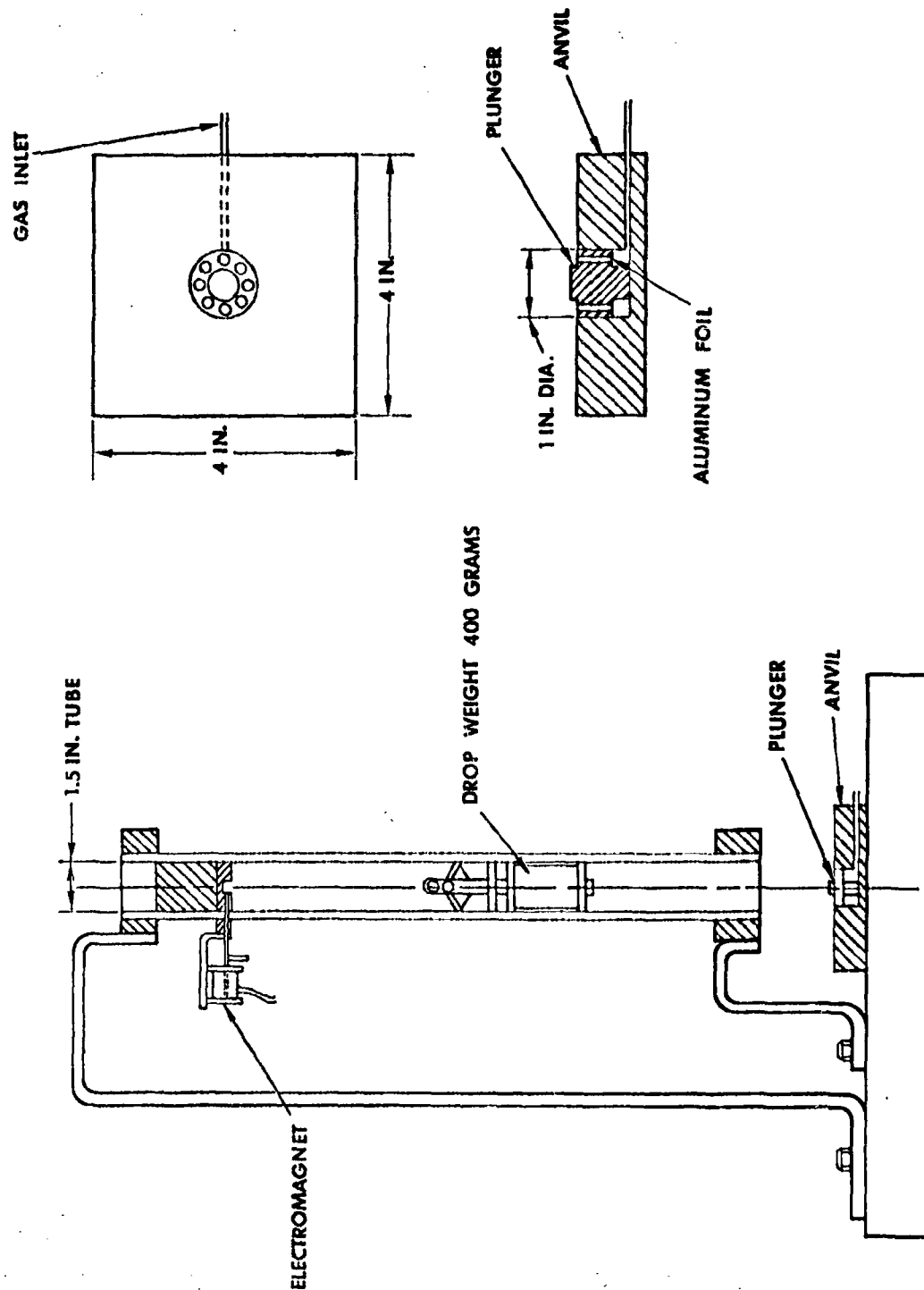
Figure 1. Drop-Weight Machine.

In part of the experiments the ambient was replaced by one of the following gases: N_2 as taken out of the bottle, N_2 purified over glowing copper chips, O_2 dried over desiccant, argon purified over glowing copper, and NO as taken out of the bottle. The chamber in the anvil was flushed for a period of 20 min. In order for the gas to reach the sample, the plunger was raised about 5 mm during flushing. In the case of NO, no flushing was done but a small amount of NO was added to the ambient.

The experiments with different gases were conducted with the machine as just described. The HP was then in contact with surfaces (anvil and plunger) of hardened steel.

Experiments were conducted with inserts of different metals between the sample and the steel surfaces. These inserts had the shape of thin wafers. The metals used are given in Table 1.

In one series of experiments, two inserts of the same metal were used. Ten tests were made with each insert. In another series, inserts of two different metals were used, one between sample and anvil, the other between sample and plunger. The case of one insert alone, the other surface being the bare anvil or the bare plunger, was included in this series. Only one test was made with each combination except for a few combinations that were tested more extensively.

3. EXPERIMENTAL RESULTS

Once the procedure for the preparation of samples was established, the spread in the sensitivity values was remarkably small. This shows first of all the uniformity of the samples. It also shows that the other variables were well controlled. A typical series is shown in Table 2.

Table 3 shows the results in various gases. It follows from these results that there is little, if any, effect of the nature of the gas under these conditions. These results are at variance with those of Bowdon et al [1,2] for liquid nitroglycerin, which show a strong dependence on the nature of the gas under similar conditions. However, it is very difficult, if not impossible, to remove all traces of air from a pile of powder without blowing the powder about. The results may therefore indicate that the gas was essentially air in all cases.

Table 1.   Test results with two inserts of various metals
in ambient air.

Metal Inserted	Thickness (in.)	Treatment	Height (cm)
None			25
Aluminum (99. 5%)	0.001	as received	>51
Aluminum (99. 99%)	0.005	as received	>51
Brass	0.003	as received	>51
Brass	0.010	as received	>51
Copper	0.010	as received	>51
Stainless 304	0.005	as received	51
Stainless 410	0.004	as received	41
Stainless 410	0.025	as received	>51
Stainless 410	0.025	short anneal	>51
Stainless 410	0.025	long anneal	>51
Steel 1095	0.005	as received	41
Steel 1095		quenched from 920°C, aged at room temperature 10 hr	28
Steel 1095		quenched from 920°C, aged at room temperature 15 min	36
Steel 1095		quenched from 920°C, tempered at 300°C, aged at room temperature 10 hr	21
Steel 1095		quenched from 920°C, tempered at 300°C, aged at room temperature 15 min	23

Table 2. Test results with two inserts of steel 1095 after quench from 920°C followed by tempering at 300°C for 1 hr and aging at room temperature for 10 hr. X= detonation, O= no detonation.

Height cm	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
38.1	X																
35.6		X															
33.0			X														
30.5				X													
27.9					X												
25.4						X											
22.9							X		X				X		X		X
20.3								O		X		O		O		O	
17.8											O						

Table 3. Test results with bare anvil and plunger surfaces and various gases.

Gas	Height cm
Ambient air	25
Dried air	25
O_2	29
"Pure" N_2	29
Dried N_2	29
NO	22
Argon	17

Table 1 shows the results with various metals, inserts of the same metal being used both below and above the sample.

Tables 4 and 5 show the results with various combinations of metals. In these tables "top" means insert of the metal in the first column between sample and plunger, "bottom" means insert of the metal between sample and anvil. Each combination was tried once only. Among these, a few were given a minimum of 10 tests in order to determine the height of detonation. The results are given in Table 5.

Table 5. Test results with inserts of different metals
in ambient air.

| Metal | | Height |
Top	Bottom	(cm)
Copper	No Insert	>51
No Insert	Copper	49
Aluminum 99.5%	Stainless 304	49
Stainless 304	Aluminum 99.5%	>51
Aluminum 99.5%	Stainless 410	>51
Stainless 410	Aluminum 99.5%	49
Aluminum 99.99%	Stainless 410	49
Stainless 410	Aluminum 99.99%	>51

4.   DISCUSSION

The results with steel are of particular interest, and these will now be discussed and then taken as reference for the results with other metals. For a discussion of the properties of the carbon steels and the effects of the various heat treatments, reference will be made to the Appendix.

Table 4. Test results with inserts of different metals in ambient air. Height 51 cm. One test with each combination. X = detonation, 0 = no detonation.

Insert	Position	No Insert	Aluminum, 99.5%	Aluminum, 99.99%	Brass, 0.003 in.	Brass, 0.010 in.	Copper	Stainless 304	Stainless 410, .004 in.	Stainless 410, .025 in.
No Insert	Top	X	X	X	X	O	X	X	X	X
	Bottom	X	X	X	X	O	O	X	X	X
Aluminum, 99.5%	Top	X	O	O	O	O	O	X	O	O
	Bottom	X	O	O	O	O	O	O	X	O
Aluminum, 99.99%	Top	X	O	O	O	O	O	O	X	O
	Bottom	X	O	O	O	O	O	O	O	O
Brass, 0.003 in.	Top	X	O	O	O	O	O	O	O	O
	Bottom	X	O	O	O	O	O	O	O	O
Brass, 0.010 in.	Top	O	O	O	O	O	O	O	O	O
	Bottom	O	O	O	O	O	O	O	O	O
Copper	Top	O	O	O	O	O	O	O	O	O
	Bottom	X	O	O	O	O	O	O	O	O
Stainless 304	Top	X	O	O	O	O	O	X	O	O
	Bottom	X	X	O	O	O	O	X	O	O
Stainless 410, 0.004 in.	Top	X	X	O	O	O	O	O	X	O
	Bottom	X	O	X	O	O	O	O	X	O
Stainless 410, 0.025 in.	Top	X	O	O	O	O	O	O	O	O
	Bottom	X	O	O	O	O	O	O	O	O

The spring steel 1095 as quenched from 920°C holds about 100 ppm of hydrogen; the same steel held at 300°C for 1 hr holds 4 ppm of hydrogen. Carbon steels of smaller carbon contents, e.g. 1042, hold less hydrogen as quenched, in proportion to the carbon content, but about the same, 4 ppm, after annealing, tempering, or aging. The quenched steel loses hydrogen by aging at room temperature, first, of course, at the surface.

The quenched spring steel insert gave a sensitivity of 36 cm some 15 min after quenching; the tempered spring steel gave a sensitivity of 24 cm 15 min after heat treatment and 21 cm 10 hr after heat treatment. This shows that atomic hydrogen in the steel affects the sensitivity. Furthermore, the quenched spring steel gave a sensitivity of 28 cm after 10 hr of aging at room temperature. This shows that the atomic hydrogen at the surface affects the sensitivity, whereas the hydrogen deeper in the metal has little effect. This conclusion is in agreement with the result with the spring steel as received, i.e., as cold rolled, that gave a sensitivity of 41 cm, less sensitivity than the quenched steel. The steel in anvil and plunger was hardened and, through use in the tests, to some extent coldworked on the surface. It had a lower carbon content, 41%, and gave a sensitivity of 25 cm.

The desensitizing effect of atomic hydrogen in the case of HP may be attributed to its opposing the oxidizing agent, the ClO_4 group. It is possible, however, that the effect pertains to intermediate reactants, e.g., those produced by the shock in the air. Further experiements will be conducted to study this effect. The chemical effect of the hydrogen is well shown in the passivation by nitric acid described in the Appendix.

The results with the spring steel inserts, and particularly a comparison between the sensitivities without insert and with insert of tempered spring steel, show that there is no appreciable mechanical effect of the insert. The inserts were thin enough to make their contribution to the acoustical impedance negligible. The reproducibility was excellent with all inserts that gave initiation, which shows that variations in geometry, e.g., flatness, had negligible effect. It may be pointed out that hardness as such does not favor initiation as shown by the low sensitivity with the quenched spring steel as compared to the same steel after tempering.

The site of the hydrogen in the quenched steel is ϵ-carbide. This carbide converts readily into cementite above 250°; hence the effect of tempering. Chromium-bearing steels hold ϵ-carbide of comparatively great stability, the transformation being inhibited by chromium. The 410 stainless steel should therefore give a sensitivity of the order of the quenched spring steel. This is in agreement with the results. The thin insert of 410 (0.004 in.) gave a sensitivity of 40 cm, and the thick insert of 410 (0.025 in.) gave one of more than 51 cm. The austenitic steel 304 may have been given a martensitic surface in cold rolling. If so, it should be comparable to the 410 steel. It gave a sensitivity of 51 cm, just at the limit of the machine.

The lowest sensitivity was given by copper and brass. With one copper insert, initiation was obtained together with the bare surface of the plunger and with no other combination. Similar cases are the combinations of aluminum and stainless steel. These four cases were checked in 10 tests with each combination. The difference between insert under and above the HP was confirmed in all these cases. These experiments will be continued in the taller machine at Chino. The present results indicate that there are two distinct phenomena in the initiation by the impact, namely, the production of shock at the surface of the plunger, and the initiation of the explosive by the shock at the surface of the anvil, and that both phenomena are affected by the metal at these surfaces. In all these cases, initiation occurred only at a height of 2 cm below the highest level. The difference between initiation and no initiation is therefore possibly no more than 2 cm. The actual difference in sensitivity will be established in the taller machine. Meanwhile it may be suggested that copper destroys the initiating property of the shock. This may be due to the reducing effect of copper so that copper has the same effect as hydrogen in quenched steel.

5. CONCLUSIONS.

There is no doubt that the sensitivity of hydrazine perchlorate to initiation by impact depends upon the nature of the metal with which it is in contact. The magnitude of the effect cannot be fully appreciated on the basis of the data available. The data show, however, that an annealed mild steel gives a sensitivity of 21 cm, whereas the same steel as cold rolled gives 41 cm, and copper gives more than 51 cm.

These results are considered promising, but further data, with a
larger range of the testing machine, are required for an estimate of
the magnitude of the effect.

The experiments with different gases around the explosive are so far
inconclusive. It is believed that this is caused by the form of the
explosive (loose powder). These experiments should be repeated with
a more suitable explosive.

6. REFERENCES

1. F. P. Bowden and A. D. Yoffee: The Initiation and Growth of
    Explosion in Liquids and Solids, Cambridge 1952.

2. F. P. Bowden and A. D. Yoffee: Fast Reactions in Solids,
    London 1958.

APPENDIX

The Effect of ε-Carbide on the Passivity of Steel in Nitric Acid Solutions.
by
T. G. Owe Berg

Summary

Carbon steels of 0.10% C, and 0.95% C were heat treated to produce ferrite + cementite, martensite, and martensite tempered at 200° C. Specimens were immersed in nitric acid solutions of various concentrations and the minimum concentration required for passivation was determined. This concentration depends upon the amount of hydrogen-rich phase, ε -carbide, in the specimen. Steel containing ferrite + cementite alone is passivated by 7.2 N acid, steel containing tempered martensite at a higher concentration, and steel containing untempered martensite at a still higher concentration. The results are related to other observations with dissolution and etching of steel in nitric acid and with ε -carbide.

1. INTRODUCTION

The various phases in steel are attacked at different rates by certain
etchants. Etching therefore gives a pattern to the etched steel
surface according to size, shape, and distribution of such phase
particles as are distinguished by the etchant.

The fact that different phases react chemically at different rates
indicates that they have different chemical compositions. Hence,
etching may be employed to show the presence of phases of known
compositions and to determine the composition of phases known to
be present.

The ideal etchant is one that attacks the phase or phases under study or
at these phases while the matrix itself is passive to the etchant. The
art of etching centers on the selection of such etchants. A particu-
larly interesting etchant for steel is concentrated nitric acid, towards
which ferrite, sustenite, and cementite are passive while certain
other phases are not.

This paper reports on experimental studies of passivity and activity
of various phases in steel towards nitric acid.

2. REACTIONS OF STEEL WITH NITRIC ACID

The mechanism of reaction of Fe with aqueous HNO_3 has been derived
from rate measurements elsewhere[1].

Armco iron and carbon steel are passive, i.e., dissolve very slowly,
in concentrated nitric acid. The passive state is preceded by a period
of dissolution, the duration of which seems to depend upon the prior
treatment of the steel. With Armco iron and annealed carbon steel,
passivity occurs above 7.16 N. At this concentration, the degree
of dissociation is $a = 2/3$, i.e., the concentration of dissociated
HNO_3 is twice that of undissociated HNO_3.

The passivation of iron and steel in HNO_3 solutions is caused by
adsorbed NO_2, nitronium, according to the formula

$$HONO_{2\ ads} \longrightarrow OH_{ads} + NO_{2\ ads}$$
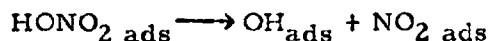
The $NO_{2\ ads}$ is decomposed to NO, nitrosyl, by certain metals, e.g., Cu, but not by other metals, e.g., Fe. For this reason, Cu dissolves rapidly in concentrated HNO_3 and at a rate proportional to the concentration of undissociated HNO_3[1]. For the same reason, Fe is passivated by undissociated HNO_3. The decomposition of $NO_{2\ ads}$ to NO_{ads} by some agent present with the Fe would cause the formation of ni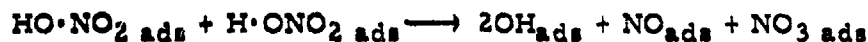trosyl compounds of Fe and thereby the dissolution of the Fe. Such agents are certain carbons and carbides[2]. Other carbides, including cementite, do not effect decomposition of $NO_{2\ ads}$ and therefore do not affect the passivity of the Fe.

The reduction of NO_2 to NO is effected by atomic hydrogen. There are reasons to believe that carbons and carbides decompose NO_2 by means of the H they contain. An H-bearing carbide destroys passivity in concentrated HNO_3, whereas an H-free carbide does not. H dissolved in Fe would have the same effect, and H-bearing Fe therefore dissolves in concentrated HNO_3 until the H concentration has been reduced sufficiently. This occurs in the period of dissolution preceding passivity. But if an H-bearing carbide is present, the H may not be removed from the carbide but continue to decompose the HNO_3 by a catalytic effect. The reaction mechanism may then be as follows

$$HO \cdot NO_{2\ ads} \longrightarrow OH_{ads} + NO_{2\ ads}$$

$$NO_{2\ ads} + H_{carbide} \longrightarrow NO_{ads} + OH_{ads}$$

$$H \cdot ONO_{2\ ads} \longrightarrow H_{carbide} + NO_{3\ ads}$$

with the net result

$$HO \cdot NO_{2\ ads} + H \cdot ONO_{2\ ads} \longrightarrow 2OH_{ads} + NO_{ads} + NO_{3\ ads}$$
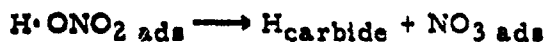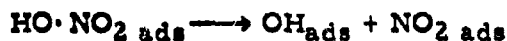
Thus, one undissociated and one dissociated HNO_3 molecule give together the formation of hydroxide, nitrosyl, and nitrate which are all soluble. The H-bearing carbide may thus cause continuous dissolution of the adjacent Fe without being attacked itself.

The H-bearing carbide of Fe is the ϵ-carbide. This carbide has been prepared and analysed with respect to H. It contains much H, and its composition is probably Fe_2HC[3]. Dissolution of steel in concentrated HNO_3 is thus indicative of presence of ϵ-carbide in the steel. Attack of steel by concentrated HNO_3 at grain boundaries is indicative of presence

of ϵ -carbide in the grain boundary material. Etching with concentrated HNO_3 is accordingly a means of detecting ϵ -carbide in steel.

Essential in this reaction mechanism is the NO_2 group of the undissociated HNO_3. The same group occurs in picric acid that is frequently used as an etchant, its composition being $(NO_2)_3C_6H_2OH$. Consequently, picric acid may also be used for detecting ϵ -carbide in steel.

In addition to these etchants, there are other acids, particularly organic acids, which require H for their reaction with Fe, e.g., for the reduction to CO and formation of carbonyl. A discussion of the reaction mechanisms of these acids would carry beyond the scope of this paper.

3. EXPERIMENTAL

Carbon steels of types 1010, 1018, and 1095 were available in sheets of approximately 1 mm thickness. Specimens were cut from these sheets, approximately 5 mm by 35 mm, and heat treated so as to produce diferent structures with different amounts of ϵ -carbide. The carbon contents of these steels are 0.10%, 0.18%, and 0.95%, respectively. The 1010 and 1018 steels were austenitized in argon at 930°C for 1/2 hr, the 1095 steel at 870°C for 1/2 hr, and then water-quenched. This treatment was designed to produce a martensitic structure. One lot was then tempered in argon at about 200°C for 2 hr and then air-quenched. This treatment was designed to produce a tempered martensite that is known to contain ϵ -carbide. Another lot was tempered in argon at 680°C for 2 hr and then air-quenched. This treatment was designed to produce ferrite + cementite free of other phases. Prior to heat treatment, a small hole was drilled at one end of each specimen so that it could be suspended in a Saran thread through the hole.

The heat treated specimens were suspended in nitric acid solutions of various concentrations in open beakers and without stirring. Specimens containing no hydrogen-rich phase should then be passivated by nitric acid above 7.16 N[1,4]. Specimens containing ϵ -carbide should, according to the mechanism outlined in Section 2, require a higher concentration of nitric acid for their passivation, depending upon the amount of ϵ -carbide present. The concentration required by each specimen for passivation to occur was determined to ± 0.05 N, the accuracy of this determination being limited by the error of titration. Passivity occurred within 20 sec or not at all, depending upon the heat treatment of the specimen and the concentration of the acid.

It is essential to the accurate determination of the concentration
required for passivation that the specimen be initially in the active
state. The specimen should therefore be immersed in an acid solution
below this concentration first and the limit be approached from the
low-concentration side. This is particularly important if the specimen
has been surface decarburized, e.g., by heating in air. The passivated
specimen can be depassivated by exposure to the air or, more quickly,
by wiping it on a towel or by scratching its surface.

The accuracy of the determination of the passivity limit was in this
experiment that of titration. Actually, the limit between passivation
and nonpassivation is much sharper. Thus, it was frequently possible
to distinguish between a fresh solution and a solution that had been used
once before and thereby slightly depleted. The reproducibility was good
to this accuracy, both with one specimen after repeated passivations
and depassivations and with several specimens from the same lot.
Somewhat surprising is that specimens of type 1095 steel heat treated on
different occasions to give a martensitic structure, one in argon and one
in air, gave the same concentration limit within the accuracy of titra-
tion. The specimens heat treated in air were surface decarburized and
therefore required to have a thin surface layer removed by abrasion or
by dissolution in low-concentration nitric acid in order to yield the same
result as the specimens treated in argon.

Table 1. Lowest normality of nitric acid at which passivation occurred.

	1010	1018	1095
Ferrite + cementite	7.2	7.2	7.5
Tempered martensite	7.3	8.0	10.0
Martensite	7.6	8.6	14.2

The "ferrite + cementite" specimens of 1010 and 1095 did not become
passive in less than 7.4 N and 7.5 N acid, respectively, when treated
as just described. This indicates that they contain some ϵ-carbide.
The specimens called "cementite + ferrite" and "martensite" were
therefore tempered at 260-270°C for 20 hr. After this treatment all
these specimens of the 1010 and 1018 steels were passivated by 7.2 N
acid.

The martensite specimens of the 1095 steel were analyzed for hydrogen by the combustion technique, using the LECO instrument for the determination of hydrogen in titanium and zirconium metals. These specimens were nearly completely martensitic. The hardness was 64 RC. Two specimens weighing 1.5720 and 1.5250 g, burned to give 1.6 and 1.3 mg of water, corresponding to 0.011 and 0.010 weight percent of hydrogen, respectively. These are comparatively high contents of hydrogen, about 100 ppm, whereas annealed steel contains of the order of 2-4 ppm. Such small amounts cannot be determined by this method of analysis. But even 100 ppm is little for a hydrogen-rich phase of stoichiometric composition. Multiplying the analysis values by 12 gives the corresponding carbon concentrations 0.14 and 0.12%, respectively. Thus, there is one H atom for every 7 or 8 C atoms.

4.   DISCUSSION

The results in Table 2 show drastic differences between the different heat treatments. At a given carbon content, "martensite" requires a much higher concentration for passivation then does "ferrite + cementite"; "tempered martensite" falls between these limits. This concentration increases with the carbon content of "martensite" and "tempered martensite" and is independent of the carbon content for "ferrite + cementite".

Tempered martensite is known to contain ϵ-carbide[5-15]. ϵ-carbide is known to contain hydrogen[3]. Hence, tempered martensite should require a higher concentration of nitric acid for passivation that does ferrite + cementite. This is in agreement with observation. But untempered martensitic specimens require still higher concentrations of nitric acid for passivation. Hence, they should contain still more hydrogen.

It may be concluded from the analysis for hydrogen in the martensitic 1095 steel that martensite does not contain hydrogen in a stoichiometric ratio, i.e., martensite is not a hydrogen-rich phase, although it may contain some dissolved hydrogen. Instead, it must be concluded, most of the hydrogen was held as ϵ-carbide. Accordingly, about 14% of the carbon in these specimens should occur as ϵ-carbide.

Hydrogen dissolved in martensite could hardly affect the passivity any more than hydrogen dissolved in ferrite. The dissolved hydrogen, whether in martensite or in ferrite, is desorbed in the active period preceding passivation. In order drastically to affect passivation, the

hydrogen must be held in a hydrogen-rich phase, e. g. , ϵ -carbide. But a hydrogen-rich phase, as distinguished from a phase holding hydrogen in solid solution, contains hydrogen in a certain stoichiometric ratio, and martensite does not. It follows that martensitic steel, whether tempered or not, contains ϵ -carbide, i. e. , martensite is partly transformed into ϵ -carbide, whether tempered or not. The results in Table 2 show then that untempered martensitic steel contains more ϵ -carbide than does tempered martensitic steel. It should be emphasized that this conclusion pertains to the specimens used in this investigation.

Tempering of martensite at and below 175°C produces changes in various properties. The magnetic intensity decreases[9, 16]. This decrease is rapid during the first few minutes and then reaches a level that depends upon the the carbon content but varies little with the temperature[9]. The c/a ratio of the martensite decreases, indicating a loss of carbon[17]. The electron microscope reveals a mottled structure after tempering at 100°C for 5 hr[5]. Carbide particles have been extracted from martensite tempered at 150°C for 170 hr. They consist of cementite; no ϵ - carbide was found with this technique[18]. After tempering above 175°C, a network of carbide has been observed at grain and subgrain boundaries[5, 6]. ϵ -carbide has been identified by X-ray diffraction in specimens tempered at about 200°C[5, 6, 10, 11].

The evidence referred to is compatible with the conclusion drawn from the results of the present investigation, namely, that both untempered and tempered martensitic steel contains ϵ -carbide, and that tempering converts this ϵ -carbide partly into cementite.

It follows from the results of this investigation and the evidence referred to that martensitic steel produced by quenching from austenite contains ϵ -carbide in fine dispersion with a particle size too small for observation and identification by conventional techniques, e. g. , electron microscopy and X-ray diffraction. Whether such martensite is invariably accompanied by ϵ -carbide will be the subject of a separate investigation. The observations made in the present investigation are not conclusive on this point. It also follows that tempering of such martensitic steel produces larger particles of ϵ -carbide, tending to agglomerate at grain and subgrain boundaries, and also causes the ϵ -carbide to convert partly into cementite.

5. APPLICATIONS

The determination of the concentration of nitric acid required for the passivation of steel is a very sensitive method for the detection and identification of ϵ-carbide. In addition, it is simple, rapid, and convenient. It supplements conventional techniques by responding to ϵ-carbide in fine dispersion. There is a quantitative relation between the concentration of nitric acid required for passivation and the amount of ϵ-carbide present. This technique will be used in further studies of ϵ-carbide in steel to be reported later. Preliminary tests indicate that it is also applicable to detection and identification of the corresponding hydrogen-rich carbide of nickel. A few other applications of the reaction mechanism outlined in Section 2 and the role of ϵ-carbide in this mechanism will be briefly mentioned.

a. Etching by Nitric Acid.

Since ϵ-carbide is an intermediate product in the formation of other carbides, ϵ-carbide should be expected to occur at the boundary between carbide precipitates and the matrix. This ϵ-carbide should then cause attack by the acid at this boundary. Sensitized stainless steel is attacked at grain boundaries such that a groove is eaten in the grain adjacent to the grain boundary. This attack indicates the presence of ϵ-carbide.

b. Temper Brittleness.

Etching with picric acid reveals grain boundaries and subgrain boundaries in temper-embrittled but not in unembrittled steel[19-21]. The embrittled steel is attacked at the grain boundaries of the primary austenite, which form the subgrain boundaries in the ferrite or martensite, and also at the ferrite grain boundaries. Addition of Nb suppresses temper brittleness and also this etch effect[21].

There is thus a correlation between temper brittleness and the etch effect and, thereby, ϵ-carbide. There are numerous observations to this effect. Thus, the susceptibility to temper brittleness increases with the carbon content[20,22]. The embrittlement occurs in the early stage of the transformation of martensite[23]. This is the stage in which ϵ-carbide appears at grain and subgrain boundaries. Nb[21,24] and Ti[25,26], which form stable carbides, suppress temper brittleness.

This correlation between temper brittleness and ϵ-carbide does not imply that presence of ϵ-carbide is a sufficient condition for temper brittleness but it does indicate that presence of ϵ-carbide is a necessary condition for temper brittleness.

It may be added that the substructure responds not only to picric acid but also to nitric acid but apparently to no other common etchant[27].

c. Stress Corrosion of Mild Steel in Nitrate Solutions.

The stress corrosion of mild steel in nitrate solutions indicates some reaction between steel and solution. This reaction should follow the mechanism for the reactions of nitric acid.

The reaction of dissociated HNO_3 on steel according to the formula

$$H \cdot ONO_{2 \text{ ads}} \longrightarrow H_{\text{metal}} + ONO_{2 \text{ ads}}$$
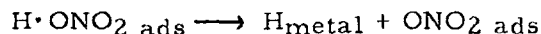
is reversible. Hence, the occurrance of nitrate on a steel surface necessarily leads to formation of nitric acid with the H in the steel, regardless of how this nitrate is formed. When immersed in a nitrate solution, the steel surface thus becomes partly covered by a mixture of absorbed HNO_3 and absorbed H_2O. This mixture is comparatively concentrated in HNO_3 and therefore contains some undissociated HNO_3. The steel surface would become passivated by this undissociated HNO_3 unless the $NO_{2 \text{ ads}}$ is reduced to NO_{ads}. This may be effected by the H in ϵ-carbide.

The gaseous products of dilute HNO_3 and C-bearing steel are NH_3, N_2, and the various oxides of N[28,29]. This shows the reduction of HNO_3 to atomic N as an intermediate and thereby the possibility of absorption of N by the steel. This reduction of HNO_3 should be accelerated by the presence of an H-rich phase in the steel. There is no formation of NH_3 or N_2 with C-free iron.

There are thus two possible roles of ϵ-carbide in the reaction of steel with a nitrate solution, namely, to destroy passivity and thereby make reaction possible, and to effect reduction of HNO_3 and thereby absorption of N.

The effect of C upon the stress corrosion of mild steel in nitrate solutions has been studied by Parkins[30]. There was a pronounced effect of the C

content upon the time to failure. Whereas cracking occured after a
few hours at a C level of 0.07% steel with 0.02% C did not fail in 500 hr.
Tempering at and above the 250°C reduced the susceptibility conspicu-
ously, tempering above 300°C reduced it to nil[31]. It follows that some
carbide is instrumental in the reaction between the steel and the nitrate
solution and that this carbide is ϵ -carbide.

It appears that the ϵ -carbide plays both roles suggested above. First
of all, it must destroy passivity, for otherwise no reaction would occur.
Second, if it causes absorption of N, the absorbed N may cause brittle-
ness and thereby stress corrosion failure. An embrittling effect of N
has been observed in numerous cases, e.g., caustic embrittlement[32,33],
that is another case of stress corrosion, and temper brittleness[25,34].
Addition of N to high-purity Fe causes intercrystalline brittleness.
Fracture in nitrate solutions is intercrystalline[36].

d.   Hydrogen-Rich Plase in Titanium.

Huber et al[37] found a phase in heat-treated Ti that was revealed by
etching with HNO_3. This phase did not occur in degassed specimens.
Radiography by means of added tritium proved that this phase is rich
in hydrogen. The conditions for its appearance suggest that it is TiN
that, according to Pollard and Woodward[38], contains H.

Acknowledgement

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